

CLAIMS

1. A process for preparing a porous film, the process comprising:
forming a composite film onto at least a portion of a substrate wherein the composite film comprises at least one structure-forming material and at least one pore-forming material; and
5 exposing the composite film to at least one ultraviolet light source within a non-oxidizing atmosphere for a time sufficient to remove at least a portion of the at least one pore-forming material contained therein and provide the porous film wherein the porous film is substantially free of Si-OH bonds.
- 10 2. The process of claim 1 further comprising treating the composite film with at least one energy source selected from the group consisting of a thermal source, α -particles, β -particles, γ -rays, x-rays, high energy electron, electron beam, ultraviolet light, visible light, infrared light, microwave, radio-frequency wavelengths, and combinations thereof.
- 15 3. The process of claim 2 wherein the at least one energy source comprises a thermal source.
4. The process of claim 1 wherein the ultraviolet light is comprised of at least one selected from the group consisting of dispersive, focused, continuous wave, pulsed, shuttered, and combinations thereof.
- 20 5. The process of claim 1 wherein the ultraviolet light has one or more wavelengths of about 340 nm or below.
6. The process of claim 5 wherein the ultraviolet light has one or more wavelengths of about 280 nm or below.
7. The process of claim 6 wherein the ultraviolet light has one or more wavelengths of about 200 nm or below.
- 25 8. The process of claim 1 wherein the ultraviolet light is at least one selected from the group consisting of an excimer laser, a barrier discharge lamp, a mercury lamp, a microwave-generated UV lamp, a picosecond or sub-picosecond laser, a frequency doubled laser in the IR or visible region, a frequency tripled laser in the IR or visible region, a two-photon absorption from a laser in the visible region, and combinations thereof.
- 30 9. The process of claim 1 wherein the exposing step is conducted in a quartz vessel, a modified deposition chamber, a conveyor belt process system, a hot

- plate, a vacuum chamber, a cluster tool, a single wafer instrument, a batch processing instrument, a rotating turnstile, and combinations thereof.
10. The process of claim 1 wherein the at least one structure-forming material is at least one selected from the group consisting of undoped silica glass (SiO_2), silicon carbide (SiC), hydrogenated silicon carbide (Si:C:H), silicon oxynitride (Si:O:N), silicon nitride (Si:N), silicon carbonitride (Si:C:N), fluorosilicate glass (Si:O:F), organofluorosilicate glass (Si:O:C:H:F), organosilicate glass (Si:O:C:H), diamond-like carbon, borosilicate glass (Si:O:B:H), phosphorous doped borosilicate glass (Si:O:B:H:P), and combinations thereof.
 11. The process of claim 1 wherein the at least one structure-forming material is represented by the formula $\text{Si}_v\text{O}_w\text{C}_x\text{H}_y\text{F}_z$ where $v+w+x+y+z=100\%$, v is from 10 to 35 atomic%, w is from 10 to 65 atomic%, x is from 5 to 30 atomic%, y is from 10 to 50 atomic%, and z is from 0 to 15 atomic%.
 12. The process of claim 1 wherein the at least one pore-forming material is selected from the group consisting of labile organic groups, solvents, polymers, surfactants, dendrimers, hyper branched polymers, polyoxyalkylene compounds, small molecules, hydrocarbon materials, and combinations thereof.
 13. The process of claim 1 wherein the at least one pore-forming precursor is selected from the group consisting of alpha-terpinene, limonene, cyclohexane, 1,2,4-trimethylcyclohexane, 1,5-dimethyl-1,5-cyclooctadiene, camphene, adamantane, 1,3-butadiene, substituted dienes, decahydronaphthelene, gamma-terpinene, alpha-pinene, beta-pinene, and combinations thereof.
 14. The process of claim 1 wherein the pore-former precursor and the structure-former precursor are the same compound.
 15. The process of claim 1 wherein the forming step involves one or more processes selected from the group consisting of thermal chemical vapor deposition, plasma enhanced chemical vapor deposition, spin coating, dip coating, Langmuir-blodgett self assembly, misting, supercritical fluid deposition, cryogenic chemical vapor deposition, chemical assisted vapor deposition, hot-filament chemical vapor deposition, and combinations thereof.
 16. The process of claim 1 wherein the exposing step is conducted during at least a portion of the forming step.

17. The process of claim 1 wherein the average size of the pores within the porous film is about 100 nanometers or less.
18. The process of claim 17 wherein the average size of the pores within the porous film is about 10 nanometers or less.
- 5 19. The process of claim 18 wherein the average size of the pores within the porous film is about 2 nanometers or less.
20. The process of claim 1 wherein the time of the exposing step is one hour or less.
21. The process of claim 20 wherein the time of the exposing step is ten minutes or less.
- 10 22. The process of claim 21 wherein the time of the exposing step is ten seconds or less.
23. The process of claim 1 wherein the at least one energy source is less than 1000 feet from the material to be exposed.
- 15 24. The process of claim 23 wherein the at least one energy source is less than 10 feet from the material to be exposed.
25. The process of claim 24 wherein the at least one energy source is less than 1 foot from the material to be exposed.
- 20 26. The process of claim 1 wherein the non-oxidizing atmosphere contains at least one gas selected from the group consisting of nitrogen, hydrogen, carbon monoxide, carbon dioxide, inert gases, and combinations thereof.
27. The process of claim 1 wherein the non-oxidizing atmosphere comprises a vacuum.
28. A process for preparing a porous film, the process comprising:
25 forming a composite film onto at least a portion of a substrate wherein the composite film comprises at least one structure-forming material and at least one pore-forming material;
 exposing the composite film to at least one energy source comprising ultraviolet light within a non-oxidizing atmosphere for a time sufficient to remove
30 at least a portion of the at least one pore-forming material contained therein and provide the porous film wherein the porous film is substantially free of Si-OH bonds; and
 treating the porous film with one or more second energy sources.

29. The process of claim 28 wherein the second energy source is at least one selected from the group consisting of a thermal source, α -particles, β -particles, γ -rays, x-rays, high energy electron, electron beam, ultraviolet light, visible light, infrared light, microwave, radio-frequency wavelengths, and combinations thereof.
30. The process of claim 28 wherein the treating step is conducted during at least a portion of the exposing step.
31. The process of claim 28 wherein the treating step is conducted prior to the exposing step.
32. The process of claim 28 wherein the treating step is conducted after the exposing step.
33. The process of claim 28 wherein the dielectric constant of the porous film after the exposing step is 2.7 or less.
34. The process of claim 28 wherein the dielectric constant of the porous film after the exposing step is 2.4 or less.
35. The process of claim 28 wherein the dielectric constant of the porous film after the exposing step is 2.2 or less.
36. The porous film prepared by the process of claim 28.
37. A process for preparing a porous film, the process comprising:
forming a composite film onto at least a portion of a substrate wherein the composite film comprises at least one structure-forming material and at least one pore-forming material; and
exposing the composite film to an ultraviolet light source within a non-oxidizing atmosphere for a time sufficient to remove at least a portion of the at least one pore-forming material contained therein and provide the porous film wherein the density of the porous film is at least 10% less than the density of the composite film.
38. A process for preparing a porous film, the process comprising:
forming a composite film having a first density onto at least a portion of a substrate wherein the composite film comprises at least one structure-forming material and at least one pore-forming material; and
exposing the composite film to an ultraviolet light source within a non-oxidizing atmosphere for a time sufficient to substantially remove the at least one pore-forming material contained therein and provide the porous film having a

second density wherein the second density is at least 10 percent less than the first density and wherein the porous film is substantially free of Si-OH bonds.

39. The process of claim 38 wherein the second density is at least 25 percent less than the first density.
- 5 40. The process of claim 38 wherein the second density is at least 50 percent less than the first density.
41. The process of claim 38 wherein the porous film is substantially the same composition as the at least one structure-forming material.
- 10 42. A chemical vapor deposition method for producing a porous film represented by the formula $\text{Si}_v\text{O}_w\text{C}_x\text{H}_y\text{F}_z$, where $v+w+x+y+z = 100\%$, v is from 10 to 35 atomic%, w is from 10 to 65 atomic%, x is from 5 to 30 atomic%, y is from 10 to 50 atomic%, and z is from 0 to 15 atomic%, the method comprising:
 providing a substrate within a vacuum chamber;
 introducing into the vacuum chamber gaseous reagents including at least one
 15 structure-forming precursor gas selected from the group consisting of an organosilane and an organosiloxane, and a pore-former precursor distinct from the at least one structure-forming precursor;
 applying energy to the gaseous reagents in the vacuum chamber to induce
 reaction of the precursors to deposit a composite film on the substrate, wherein the
 20 composite film comprises at least one structure-forming material and at least one pore-forming material; and
 exposing the composite film to an ultraviolet light source within a non-oxidizing atmosphere for a time sufficient to substantially remove the at least one pore-forming material contained therein and provide the porous film comprising a plurality of pores and
 25 a dielectric constant of 2.7 or less wherein the porous film is substantially free of Si-OH bonds.
43. The method of claim 42 wherein the organosilane is at least one member selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane, tetramethylsilane, phenylsilane, methylphenylsilane,
 30 cyclohexylsilane, tert-butylsilane, ethylsilane, diethylsilane, tetraethoxysilane, dimethyldiethoxysilane, dimethyldimethoxysilane, dimethylethoxysilane, methyldiethoxysilane, triethoxysilane, trimethylphenoxysilane, phenoxysilane, diacetoxymethylsilane, methyltriethoxysilane, di-tert-butylsilane, and combinations thereof.

44. The method of claim 42 wherein the organosiloxane is at least one member selected from the group consisting of 1,3,5,7-tetramethylcyclotetrasiloxane, octamethylcyclotetrasiloxane, hexamethylcyclotrisiloxane, hexamethyldisiloxane, 1,1,2,2-tetramethyldisiloxane, octamethyltrisiloxane, and combinations thereof.
45. The method of claim 42 wherein the pore-former precursor is at least one member selected from the group consisting of alpha-terpinene, limonene, cyclohexane, 1,2,4-trimethylcyclohexane, 1,5-dimethyl-1,5-cyclooctadiene, camphene, adamantane, 1,3-butadiene, substituted dienes, gamma-terpinene, alpha-pinene, beta-pinene, decahydronaphthelene, and combinations thereof.
46. A porous film comprising a dielectric constant of 3.5 or below, the porous film comprising:
at least one structure-forming material comprising Si, C, H, and O;
at least one pore-forming material consisting essentially of C and H; and
a plurality of pores having an average size of about 100 nm or less
wherein the plurality of pores are formed by removing at least a portion of the pore-forming material by exposure to an ultraviolet light source to provide the porous film wherein the porous film is substantially free of Si-OH bonds.
47. The porous film of claim 46 wherein the structure-forming material is comprised of a compound having the formula $\text{Si}_v\text{O}_w\text{C}_x\text{H}_y\text{F}_z$, where $v+w+x+y+z = 100\%$, v is from 10 to 35 atomic%, w is from 10 to 65 atomic%, x is from 5 to 30 atomic%, y is from 10 to 50 atomic%, and z is from 0 to 15 atomic%.
48. The porous film of claim 46 wherein the amount of the pore-forming material within the porous film is about 5 weight % or less of the overall weight of the pore-former material in the film prior to exposure to the ultraviolet light source.
49. The porous film of claim 46 wherein the amount of the pore-forming material within the porous film is about 0.5 weight % or less of the overall weight of the pore-former material in the film prior to exposure to the ultraviolet light source.
50. The porous film of claim 46 having a compositional non-uniformity of about 10% or less.
51. A mixture for depositing an organosilicate film, the mixture comprising at least one structure-former precursor selected from the group consisting of an organosilane and an organosiloxane and a pore-former precursor wherein at

least one precursor and/or the organosilicate film exhibits an absorbance in the 200 to 400 nm wavelength range.

52. A mixture for depositing an organosilicate film, the mixture comprising: from 5 to 95% by weight of a structure-former precursor selected from the group consisting of an organosilane and an organosiloxane and 5 to 95% by weight of a pore-former precursor wherein at least one of the precursors and/or the organosilicate film exhibits an absorbance in the 200 to 400 nm wavelength range.

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